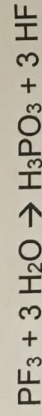## [1] Reactions in solutions: acid-base titrations (12 pts)

[1](a) Phosphorus trifluoride (PF_3) is a highly toxic gas that reacts slowly with water to give a mixture of phosphorous acid (H_3PO_3) and hydrofluoric acid (HF). The balanced chemical equation for this reaction is:

$$PF_3 + 3 H_2O \rightarrow H_3PO_3 + 3 HF$$

Please determine the concentration of each of the acids that result from the complete reaction of 1.94 L of PF_3 (measured at 25°C and 0.970 atm pressure; PF_3 is in gaseous phase at this P-T) with enough water to give a solution volume of 872 mL.

$$PV = nRT \qquad \frac{0.970 \times 1.94}{0.08206 \times 298.15} = n = 0.0769 \text{ mol } PF_3$$

$P = 0.970$
$T = 298.15 \text{ K} = 25°C$
$V = 1.94 \text{ L}$
$n = ?$

$= 0.0769 \text{ mol } H_3PO_3$

$1 : 1 : 3 \qquad = 3(0.0769) \text{ mol } HF$
$\qquad = 0.2307 \text{ mol } HF$ ✓

$Volume = 0.872 L = 872 \text{ ml}$

$CoC = \frac{mol}{Vol} \qquad CoC \ HF = \frac{0.2307}{0.872} = 0.265 \text{ M } HF$

$Conc \ H_3PO_3 = \frac{0.0769}{0.872} = 0.0882 \text{ M } H_3PO_4$

[1](b) To determine the concentration of a sample solution of nitric acid (HNO_3), a 100.0-mL sample is placed in a flask and titrated with a 0.1279 M solution of KOH (aq). A volume of 37.85 mL KOH (aq) is required to reach the phenolphthalein end point. Please calculate the concentration of nitric acid in the original sample.

$$HNO_3 + KOH \rightarrow KNO_3 + H_2O$$

M_A ?
$V_A \ 0.1 L$
$M_B \ 0.1279 M$
$V_B \ 0.03785 L$
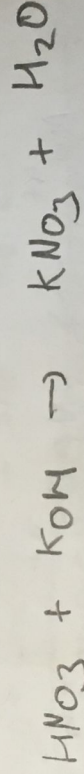
$M_A V_A = M_B V_B \qquad Conc \times vol = mol$

$M_A \times 0.1 L = 0.1279_M \times 0.03785 L$

$M_A \times 0.1 L = 0.004846 = 0.00484$

$M_A = \frac{0.00484}{0.1 L} = M_A = 0.0484 M$

$H_2O \ HNO_3 \ CoC = 0.0484 M$

12

[2] Reactions in solutions: redox titrations (12 pts)
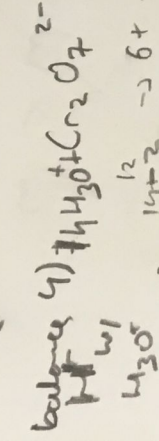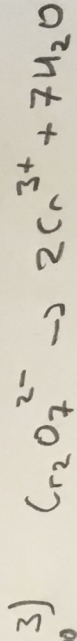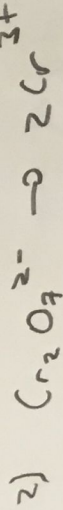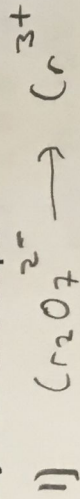
For the following redox reaction between dichromate ($Cr_2O_7^{2-}$) ions and neptunium (IV) ions, Np^{4+}, in an acidic solution:

$$\underset{+6}{Cr_2O_7^{2-}}(aq) + \underset{+4}{Np^{4+}}(aq) \longrightarrow \underset{+3}{Cr^{3+}}(aq) + \underset{+6}{NpO_2^{2+}}(aq)$$
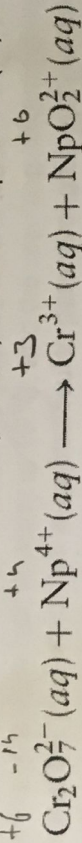
[2](a) Please follow the 6 steps listed in the formula sheet to balance this oxidation-reduction reaction. **Please clearly show all 6 steps.**

1) $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ $Np^{4+} \longrightarrow NpO_2^{2+}$ half rxn

2) $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$ $Np^{4+} \longrightarrow NpO_2^{2+}$ 6oxy't'ct'y

3) $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$ $2H_2O + Np^{4+} \longrightarrow NpO_2^{2+}$

Balancing O w/H₂O

Balance 4) $14H_3O^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O + 14H_2O$ $6H_2O + Np^{4+} \longrightarrow NpO_2^{2+} + 4H_3O^+$

H w/ H₃O⁺

5) $6e^- + 14H_3O^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 21H_2O$ $6H_2O + Np^{4+} \longrightarrow NpO_2^{2+} + 4H_3O^+ + 2e^-$

Balance charge

$14\,e^- - 2 \longrightarrow 6^+ + 6e^-$ $2e^- 4^+ \longrightarrow 6^+$

6) $6e^- : 2e^-$
   $\quad\quad 6 : 2$
   $\times 1 \quad\quad \times 3$

$6e^- + 14H_3O^+ + Cr_2O_7^{2-} + 18H_2O + 3Np^{4+} \longrightarrow 2Cr^{3+} + 2\frac{1}{2}H_2O + 3NpO_2^{2+} + 12H_3O^+ + 6e^-$

$2H_3O^+ + Cr_2O_7^{2-} + 3Np^{4+} \longrightarrow 2Cr^{3+} + 3NpO_2^{2+} + 3H_2O$ ✓

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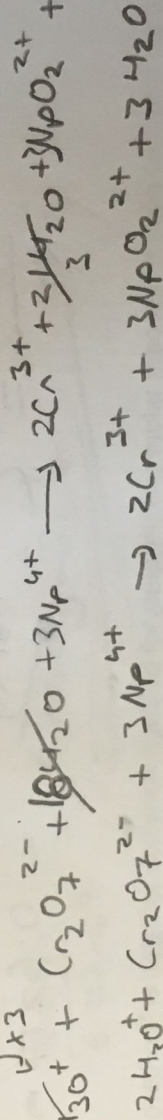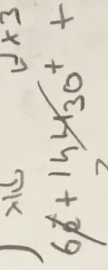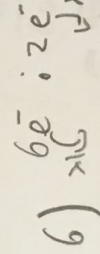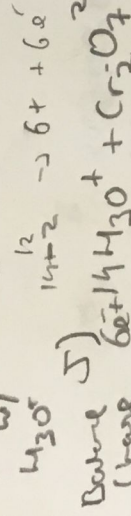
[2](b) A sodium dichromate ($Na_2Cr_2O_7$) solution is prepared by dissolving 5.000 g of $Na_2Cr_2O_7$ in water and diluting to a total volume of 50.00 mL. A total of 32.50 mL of this solution is required to reach the end point in a titration of 100.0-mL sample containing Np^{4+} (aq). Please calculate the concentration of Np^{4+} in the original solution.

$$\frac{5.000g}{M_{Na_2Cr_2O_7}} = \frac{5}{261.9478} = 0.01909 \text{ mol } Na_2Cr_2O_7$$

$$\frac{0.01909 \text{ mol}}{0.050 L} = M = 0.3817 M$$

$$32.50 mL = 0.03250 L$$

$$0.3817 M \times 0.03250L = \text{mol } Na_2Cr_2O_7$$
$$= 0.01241 \text{ mol } Na_2Cr_2O_7$$

$$0.01241 \text{ mol} \times 3 = n(Np^{4+}) \quad\quad Na_2Cr_2O_7 : Np^{4+}$$
$$= 0.03722 \text{ mol } Np^{4+} \quad\quad 1 : 3$$ ✓

Vol $Np^{4+} = 0.11 L$

$$C_{oc} = \frac{mol}{Vol} = \frac{0.03722}{0.1} = 0.3722 \text{ mol/L } Np^{4+}$$

12
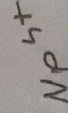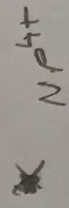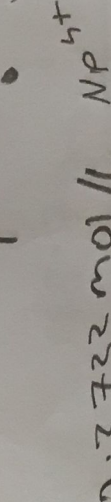
[3] Phase equilibrium in solutions (12 pts)

[3](a) A common way to determine the molar mass of a dissolved substance is through its osmotic pressure. A polymer of large molar mass is dissolved in water at 15 °C, and the resulting solution rises to a final height of 15.2 cm above the level of the pure water, as water molecules pass through a semipermeable membrane into the solution. If the solution contains 4.64 g polymer per liter, please calculate the molar mass of the polymer.

$$T = 288.15 \, K$$

$$h = 0.152 \, m \qquad \rho = 196^{-3} = 1 \times 10^3 \, kg/m^3$$

$$\Pi = \rho g h = 1 \times 10^3 \times 9.8 \times 0.152 = 1489.6 \, kg/m^3$$

Clash

$$\frac{kg/m^2}{/1000} \qquad \frac{?}{/1000}$$

$$\Pi = CRT \qquad \frac{\Pi}{RT} = C = 0.6217 \, mol/m^{-3} = @ 6.217 \times 10^{-4} \, M$$

$$Conc = \frac{mol}{vol = 1} = \frac{mol}{1} = mol \qquad mol = \frac{mass = 4.64}{Mr = x} = \frac{4.64}{x}$$

$$\frac{4.64}{Co - C} = conc$$

$$\frac{4.64}{6.217 \times 10^{-4}} = 7,462.8 \, g \, mol^{-1} \qquad 6 \cdot 6$$

[3](b) "The Rast method" is another common method for determining molar masses. It uses camphor as the solvent. Camphor melts at 178.4 °C at 1 atm, and its large freezing-point depression constant, $K_f = 37.7$ K kg mol⁻¹, makes it especially useful for accurate work. A sample of an unknown substance that weighs 0.840 g reduces the freezing point of 25.0 g of camphor to 170.8 °C. Assume this substance dissolves in camphor but not dissociates. What is its molar mass?

$$T_f = 178.4 °C = 451.55 \, K \qquad Mr \, ? = x \qquad x = \frac{mol \, solute}{kg \, solv}$$

$$\Delta T_f = 170.8 - 178.4 = -7.6 \, K$$

$$\Delta T_f = 170.8 - 178.4 = -7.6 \, K$$

$$\Delta T_f = -K_f \cdot m \qquad -7.6 = (37.7 \, kkg) \qquad \frac{9.2}{?} \qquad 6 \cdot 6$$

$$0.20159 = molal.$$

$$molal = \frac{0.840/x}{0.025 \, kg \, camphor} \qquad 0.20159 \times 0.025 = \frac{0.840}{x}$$

$$0.840 \, g \qquad x = 166.67 \, g \, mol^{-1}$$

$$\frac{0.840 \, g}{0.005039 \, mol} = x = 166.67 \, g \, mol^{-1}$$

$$\underline{166.7 \, g \, mol^{-1}}$$

+14

[4] The first law of thermodynamics: ideal gas processes (part I) (14 pts)

A system containing 2 mol of a monoatomic ideal gas is taken through the cycle in the right diagram in the direction indicated by the arrows: an **adiabatic reversible expansion** from state 1 to state 2, an **isochoric (constant V) heating** from state 2 to state 3, and an **isothermal reversible compression** from state 3 back to state 1. Let's work on this ideal gas cycle in questions [4] and [5].
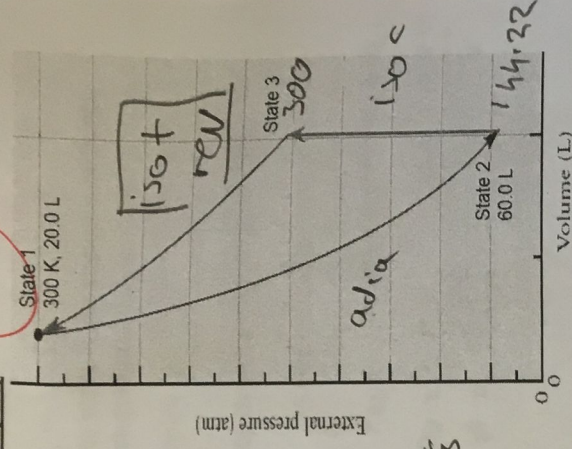
[4](a) Please calculate the temperature of this monoatomic ideal gas system at state 2, T_2. (Hint: state 1 to state 2 is an **adiabatic reversible process**; you can also find useful information on the diagram.)

$T_1 = 300K, V_1 = 20.0 L \qquad \gamma - 1 = \dfrac{c_p}{c_v} - 1$

$$= \dfrac{5/2}{3/2} - 1 = \dfrac{2}{3}$$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$300 \times 20^{2/3} = (T_2)(60)^{2/3}$

$\dfrac{2 \cdot 10}{60^{2/3}} = T_2 \qquad T_2 = 144.22 K$

---

[4](b) Please calculate q, w, ΔU, and ΔH for this **adiabatic reversible expansion** from state 1 to state 2.

adiabatic : $q = 0$

$\Delta H = n c_p \Delta T$

$\Delta U = n c_v \Delta T \qquad \Delta U = q + w$

$w = n c_v \Delta T$

$T_2 - T_1 = 144.22 - 300 = -155.78$

$\Delta H = 2 \times \dfrac{5}{2} \times 8.3145 \times -155.78 = -6476 J$

$\Delta U = 2 \times \dfrac{3}{2} \times 8.3145 \times -155.78 = -3885.69 J$

$w = \Delta U = -3885.7 J$

---

[4](c) Please calculate q, w, ΔU, and ΔH for the **isochoric heating** from state 2 to state 3.

Iso Choric $\Delta V = 0 \qquad w = 0$

$T_f = 300K \quad T_i = 144.22 k$

$\Delta U = q + w$

$\Delta U = q = n c_v \Delta T$

$\Delta H = n c_p \Delta T$

$q = n c_v \Delta T$

$\Delta U = 2 \times \dfrac{3}{2} \times 8.3145 \times (300 - 144.22 k)$

$\Delta U = 3885.69 J = q = 3885.69 J$

$\Delta H = 2 \times \dfrac{5}{2} \times 8.3145 \times (300 - 144.22)$

$= 6476 J$

$w = 0$

[5] The first law of thermodynamics: ideal gas processes (part II) (14 pts)

(Continued from [4])

[5](a) Now let's focus on the **isothermal reversible** compression from state **2** to state **1**. As shown in lectures and review sessions for a few times, the work done by the gas in this process should be:

$$w = -nRT \ln \frac{V_2}{V_1}$$

Please derive this equation, starting with $w = -\int_{V_1}^{V_2} P_{ext} dV$. **Please clearly write down every step in this derivation.**

$3 \to 1$ (circled, red)

isothem,

$\Delta U = 0 \quad -q = w \quad w = -P_{ext} dV \quad w = \int_{v_1}^{v_2} dw$

$$w = -\int_{v_1}^{v_2} P_{ext} dV \qquad P_{ext} = P_{\text{reversible}}$$

$$= -\int_{v_1}^{v_2} P \, dV \qquad PV = nRT \quad -P = -nRT$$

$$= -\int_{v_1}^{v_2} \frac{nRT}{V} dV \qquad P = \frac{nRT}{V} \qquad -P = \frac{-nRT}{V}$$

$$= -nRT \int_{v_1}^{v_2} \frac{1}{V} dV$$

$$= -nRT \ln\left(\frac{v_2}{v_1}\right) = nRT \ln\left(\frac{v_1}{v_2}\right)$$

$$q = nRT \ln\left(\frac{v_2}{v_1}\right)$$

[5](b) Please calculate q, w, ΔU, ΔH, and **ΔS** (circled) for this **isothermal reversible** compression from state 2 to state 3.

$$\Delta U = 0 = 5480 - 5480 \qquad 3 \to 1 \qquad V_2 = 20L \qquad T = 300$$
$$\Delta H = 0 = 0 + 0 \qquad V_1 = 60L$$

$$q = nRT \ln \frac{v_2}{v_1} \qquad q = nRT \ln \frac{v_2}{v_1} = 2 \times 8.3145 \times 300 \times \ln\left(\frac{20}{60}\right)$$

$$q = -w \qquad w = -nRT \ln \frac{v_2}{v_1} \qquad q = -5480.65 J$$

$$\Delta S = \frac{q}{T} = \frac{nRT \ln \frac{v_2}{v_1}}{T} \qquad = -2 \times 8.3145 \times 300 \times \ln\left(\frac{20}{60}\right)$$

$$= nR \ln \frac{v_2}{v_1} \qquad w = 5480.65 J$$

$$= 2 \times 8.3145 \times \ln\left(\frac{20}{60}\right) = -18.27 J k^{-1}$$

[5](c) Combine your answers in [4](c), [5](a), and [5](b), please calculate q, w, ΔU, and ΔH for the entire cycle. (Hint: the change of a state function for the entire cycle should be?)

State function:

$$\Delta U = 0 = -3886 J + 3886 J = 0$$
$$\Delta H = 0 = -6476 J + 6476 J = 0$$

$$q = 0 + 3885.69 J + -5480.65 J = -1594.96 J$$

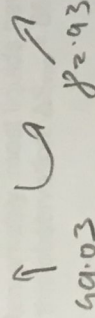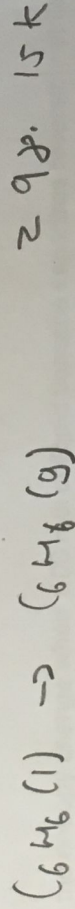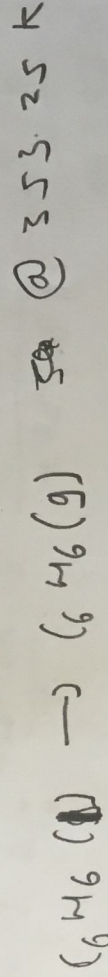$$w = -3885.69 J + 0 + 5480.65 J = 1594.96 J$$

$+14$ (circled, red)

$-hof.U$ (red)

[6] Thermochemistry (12 pts)

Using the information provided below, please calculate the enthalpy change for the reaction:

benzene (l) → benzene (g)

at its normal boiling point (80.1 °C and 1 atm). You can treat the molar heat capacities as temperature-independent.

Substance	ΔH_f° (25°C) kJ mol⁻¹	S° (25°C) J K⁻¹ mol⁻¹	ΔG_f° (25°C) kJ mol⁻¹	C_P (25°C) J K⁻¹ mol⁻¹
$C_6H_6(g)$	82.93	269.2	129.66	81.6
$C_6H_6(\ell)$	49.03	172.8	124.50	136

298 k

$C_6H_6 (\ell) \longrightarrow C_6H_6(g)$ Δ_a @ 353.25 k

293.25 k

$q_{P_1} \downarrow$ $\uparrow q_{P_2}$

$C_6H_6 (\ell) \longrightarrow C_6H_6(g)$ 298.15 k

49.03   82.93

q

$q_{P_1} = nc_P\Delta T = 1 \times 136 \times (t_2 - T_i) = 136 \times (298.15 - 353.25)$
(L)
$= 136 \times -55.1 = -7493.6 J$

$q_{P_2} = nc_P\Delta T = 1 \times 81.6 \times (353.15 - 298.15)$
(g)
$81.6 \times 55.1 = 4496.16 J$

q

$\Delta H = \sum n_i \, Products - \sum n_i \, reactants = 7 \times 82.93 - 1 \times 44.03$
$= 33.9 \, kJ$

$q_{P_1} + \Delta H + q_{P_2} = \Delta H_{input} \, 353.25 k$ $33900 J$

$-7493.6 J + 4496.16 J + 33.9 \, kJ$

$-7493.6 J + 4496.16 J + 33,900 J = 30,902.56 J$

$= 20.9 \, kJ$

[7] The second and third laws of thermodynamics (8 pts)

When heating 1.00 mol of **solid benzene** from 5.53 °C to 80.1 °C at 1 atm to reach a final state of **completely gaseous benzene**, it undergoes two phase transitions: melting (at 5.53 °C) and evaporation (at 80.1 °C). The molar enthalpy of fusion of benzene at its normal melting point is 9.9 kJ mol⁻¹, and you have calculated the molar enthalpy of vaporization at its normal boiling point in [6].

[7](a) Please calculate the entropy change when 1.00 mol of solid benzene melts reversibly at its normal melting point, ΔS_{fus}.

$$q + \frac{\Delta H}{T} + q$$

$$9.9kJ = 9900 \, J$$
$$5.53°C = 278.68k$$

$$\Delta S = \frac{q_{rev}}{T} \quad \Delta S_{fus} = \frac{n \times \Delta H_{fus}}{T_f} = \frac{1 \times 9900 \, J \, mol^{-1}}{278.68k}$$

$$= 35 \, J \, K^{-1}$$

$$\underline{35 \, 35 \, J \, K^{-1}}$$

[7](b) Please calculate the entropy change when 1.00 mol of liquid benzene vaporizes reversibly at its normal boiling point, ΔS_{vap}. (Hint: Remarkably, most liquids have similar values for the molar entropy of vaporization. Trouton's rule summarizes this observation: ΔS_{vap} = 88 ± 5 J K⁻¹ mol⁻¹) $T_b = \cancel{80.1} \, 80.1°C = 353.25k$

$$\Delta S = \frac{q_{rev}}{T} \qquad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \qquad \text{4/4}$$

$$\Delta S_{vap} \times T_b = \Delta H_{vap} \times 1 \, mol$$

take ΔS_{vap}
to be $88 \pm 5 \, J \, K^{-1} \, mol^{-1}$ $88 \, J \, K \, mol^{-1} \times 353.25 = 31,086 \, J$
by Trouton's rule
$$= 31,086 \, kJ$$

using
Trouton's (b) $= 31.086 \, kJ$

$$\Delta S = 87.48 \, J \, K^{-1} \qquad (\pm \, 1766.25 \, J)$$

$$= \qquad ([J \, s])$$

$$\Delta H_{vap} = 30.9 \, kJ \, mol^{-1} \qquad \qquad \Delta H_{vap} = 30.9 \, kJ$$

$$\Delta S = \frac{\Delta H_{vap n}}{T} = \frac{30.9 \, kJ \times 1000 \times 1 \, mol}{} = 87 \, J \, k^{-1} \qquad \therefore \, correct$$

$$\frac{30,900 \, J}{353.25k} = \Delta S \approx 88 \pm 5 \, J \, k \, mol^{-1}$$

mol Answer

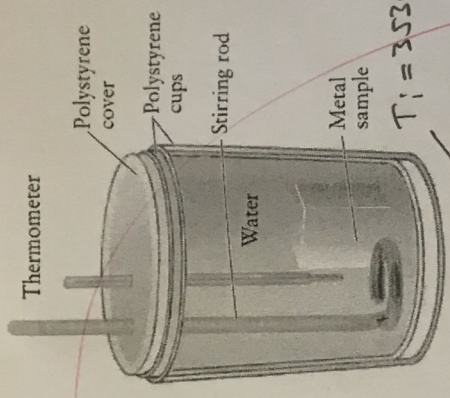$$\underline{\frac{30,900 \, J}{353.25k}}$$

— Prof. U

[8] Entropy changes and spontaneity (14 pts)

From our daily life experience, we know that when a hot body contacts with a cold body, heat will spontaneously flow from the hot body to the cold body, until the temperature of the two bodies reaches the same (thermal equilibrium). Let's use the following example to find the driving force of this spontaneous process.

[8](a) A piece of iron weighing 50.0 g is heated to 80 °C and plunged into 100.0 g water that is initially at 10 °C in a Styrofoam cup calorimeter. Assume no heat is lost to the Styrofoam cup or to the environment. Please calculate the final temperature that is reached. Please take $c_{P,m}$ (Fe) to be 25.1 J K^{-1} mol^{-1} and $c_{P,m}$ (H_2O) to be 75.3 J K^{-1} mol^{-1}, independent of temperature.

$$using \ nc_P \Delta T = q_P$$

$$g \rightarrow mol$$

$$mol \ Fe = \frac{50g}{55.845} = 0.895 \ mol/Fe \qquad T_i = 353.15k$$

$$mol \ H_2O = \frac{100g}{18.0152} = 5.55 \ mol \ H_2O$$

$$T_i = 283.15$$

Fe: $0.895 \times 25.1 \times (T_f - 353.15)$

$-(22.473 (T_f - 353.15))$

$H_2O = 5.55 \times 75.3 (T_f - 283.15)$

$\frac{417.98 (T_f - 283.15)}{}$ ✓ 5/5

$417.98 (T_f - 283.15) = -22.473 (T_f - 353.15)$

$417.98 T_f - 118351 = -22.473 T_f + 7935$ ✓ 5/5

$\frac{126287}{440.457} = \frac{126287}{440.457} = 286.72k$ ✓

$440.457 T_f = 126287 \qquad T_f = 286.72k$

$$Fe = \sim H_2O$$

[8](b) Please calculate the entropy change for the iron, ΔS_{Fe}, the entropy change for the water, ΔS_{H2O}, and ΔS_{tot} in this process.

$$S_{y} \rightarrow \Delta S_{Fe} = \frac{q_{rev}}{T} = \frac{q_P \ entrop}{T} = nc_P \ln \frac{T_2}{T_1}$$

$$= 0.895 \times \ln \left(\frac{286.72}{353.15} \right) \times 25.1 \ JK^{-1}$$

$$S_y \rightarrow \Delta S_{H2O} \approx \frac{-\Delta H}{T} = nc_P \ln \frac{T_2}{T_1} = 5.55 \times \& 75.3 \ JK^{-1} mol^{-1} \times \ln \left(\frac{286.72}{283.15} \right)$$ ✓

$$\Delta S_{Fe} = -4.68 \ JK^{-1} \qquad \Delta S_{H2O} = 5.236 \ JK^{-1}$$ ✓

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = -4.68 + 5.236 = 0.555 \ JK^{-1}$$

[8](c) Is this cooling process of iron spontaneous? Please reason your answer using your calculation in [8](b).

This Process is Spontaneous, when $\Delta S_{tot} > 0$, the process is spontaneous of $\Delta S_{tot} = 0$, process is ✓

Question	Points earned	Question	Points earned	Question	Points earned
0	2/2	3	12/12	6	12/12
1	12/12	4	14/14	7	18/18
2	12/12	5	14/14	8	14/14
				Total	100/100

PERFECT! Hearty congrats, Henry!
— Prof. U